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University of Toronto

LABORATORY EXERCISES IN ELECTROCHEMISTRY

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ELECTROCHEMICAL LABORATORY

Ten laboratory exercises to accompany the course of lectures on Elementary Electrochemistry.

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University of Toronto

ELECTROCHEMICAL LABORATORY

GENERAL REGULATIONS

Return of Apparatus.—The apparatus needed for each day's work will be found at the student's working place, clean and ready for use; with it is a list, which should be checked over. At the close of the exercise the glass apparatus should be cleaned and collected together, and the burettes and pipettes filled with chromic acid mixture; each student should sign the list, noting any breakages, and leave it with the apparatus.

All wires should be left neatly coiled, as found; and in particular *all connections to the terminal boards must be broken;* neglect of this precaution may lead to serious damage. A fine of one dollar is imposed for the first offence against this regulation, and five dollars for the second.

Care of Instruments.—The cost of repairing damage to instruments will be charged against the student or group of students responsible.

In setting up circuits the connections to the terminal board must be made *last,* after the other connections have been checked over.

One of the wires of the 110 volt supply is grounded; if a lead from the other wire should accidentally come in contact with a gas pipe or water pipe an accident might ensue, perhaps an instrument might be burned out.

The chemicals with which the student works are a special source of danger. Acids, salt solutions, etc., on the hands or spilled on the table may easily get on the instruments, on books, or on the clothes. Every working place is provided with a sink and towels; any chemicals spilled should be cleaned up immediately.

Iodine, Silver, and Mercury residues.—On each table receptacles are provided for waste liquids, etc., containing iodine, silver, or mercury respectively; all such residues should be poured into the proper receptacle and not down the sink. At the end of the term these wastes are worked up and the values recovered.

Care of Sinks.—Mercury and its salts are particularly destructive to lead, and should never be allowed to get into the sinks. Receptacles are provided on each table to collect used mercury, calomel, and solutions containing mercury salts; there is thus no excuse for throwing them into the sinks.

A fine of one dollar is imposed for the first offence against this regulation, and five dollars for the second. If the offender can not be identified, every student working at the damaged sink must pay the full fine. This regulation will be strictly enforced; its object is to ensure the active coöperation of every man in the laboratory in keeping mercury out of the sinks; the money collected does not nearly pay for the damage done.

Reports.—At the beginning of every laboratory period the instructor in charge will outline the work to be undertaken, emphasize the precautions necessary, and indicate the nature of the report to be sent in. The best place and time for writing out the report is *in the laboratory while the work is going on;* the result of every measurement should be entered in the final report as soon as it is obtained, not merely jotted down on a scrap of paper.

If he prefers, however, a student may write his report at home, and hand it in on the day of the next exercise (not later); such delayed reports must be distinctly better written than those made at the time, if they are to obtain the highest rating.

Paper and covers for the reports are provided in the laboratory and are charged to the student's account.

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EXERCISE 1

(A) VOLUMETRIC DETERMINATION OF FREE IODINE

Iodine dissolves in an aqueous solution of potassium iodide to form a brown liquid which is decolorized by addition of sodium thiosulphate. It has been found that if the solution be neutral or slightly acid the amount of thiosulphate necessary to bleach it is proportional to the amount of iodine dissolved, one gramme of the latter requiring 1.247 g. anhydrous sodium thiosulphate[1] $Na_2S_2O_3$, as represented by the chemical equation:

$$I_2 + 2Na_2S_2O_3 = Na_2S_4O_6 + 2NaI.$$

Thus by determining the amount of sodium thiosulphate needed to remove the coloration, the amount of iodine dissolved may be found. Note that the amount of thiosulphate needed is independent of the amount of potassium iodide in the solution; only "free iodine", not "total iodine" is determined by this method.

If a solution of sodium thiosulphate containing a known weight of that salt per litre be prepared, it is only necessary to find the *volume* of the solution needed to bleach the iodine solution; the method thus becomes one of "volumetric analysis." The "volumetric" thio. solution usually employed contains $\frac{1}{10}$ of 158.2 g. of $Na_2S_2O_3$[2] per litre, and is known as "decinormal" or "tenth-normal" (N/10) solution, the normal solution containing 158.2 g. thiosulphate per litre. One litre of normal solution thus bleaches, or "is equivalent to," 126.9 g. iodine, the amount represented by the chemical symbol I. Similarly a solution containing 126.9 g. iodine per litre is a "normal" iodine solution.

---

[1] *The student should verify this.*

[2] $2 \times 23.05 + 2 \times 32.06 + 3 \times 16 = 158.22$. *Crystallized thiosulphate* $Na_2S_2O_3\ 5H_2O$ *is used in making up the solutions; 1/10 of 248.4 g. must be taken (verify!) Unfortunately, the commercial salt is not absolutely pure, so solutions made from it must be "standardized" by comparison with a solution of iodine prepared for the purpose with precautions detailed in books on chemical analysis. Moreover, the "thio" solution undergoes slow decomposition on keeping, so the standardization must be repeated from day to day. The solutions provided have been so standardized.*

1

Comparison of Volumetric Iodine and Thio. Solutions

Fill one of the burettes.[1] preferably the right hand one, with the volumetric thio, and the other with the volumetric iodine solution. See that the stopcocks are completely filled with solution (why?), then note the "reading" of each burette. In the case of colourless solutions, like the thiosulphate, it is well to hold a piece of white paper at the back of the burette; the bottom of the meniscus then appears as a sharply defined black line across the divisions of the burette. The dark colour of the iodine solution makes it more convenient to read the top of the meniscus; to avoid parallax always keep the eyes at the level of the meniscus.

Titration

Run about 20 c.c. of the iodine solution into a beaker, and then thio, with constant stirring. The brown colour will fade to a pale yellow and then disappear. If a few drops of starch solution be added to the solution in the beaker, while still slightly yellow, it will turn a deep blue; this makes it very easy to recognize the "end-point." The starch is spoken of as an "indicator" for iodine; it must not be added until the end-point is almost reached.

To make sure that too much thio has not been used, add the iodine drop by drop until the blue colour is restored ("titrating back"); it must then be bleached again by one drop of thio. Now read the burettes again.

Calculation

The readings should be entered in the reports as in the following example:

	Iodine		*Thio.*
	0.00		0.25
	20.45		21.60
	20.45 c.c.	=	21.35 c.c.
Therefore,	1.00 c.c.	=	1.044 c.c.

The iodine is thus "stronger" than the thio. If the latter be exactly N/10, the iodine will be 0.1044 normal, and each litre will contain 0.1044×126.9=13.24 g. iodine.

Determination of Free Iodine

By means of these solutions unknown quantities of free iodine may be determined. Dissolve, if necessary, in potassium iodide solution (need the quantity of iodide be known?); run in thio until light yellow, add starch, then thio again till colourless. *Make sure of the end point* by titrating back with volumetric iodine.

---

[1] *Before filling a burette rinse it out with about 5 c.c. of the solution it is to contain. Each student is provided with small labelled flasks to hold the volumetric solutions; these should be filled from the stock bottles, after rinsing each with five or ten c.c. of the solution it is to contain. The burettes are then to be filled at the student's working place. NO RINSINGS OR RESIDUES MAY BE POURED BACK INTO THE STOCK BOTTLES.*

Example:

$$
\begin{array}{lcl}
\textit{Iodine} & & \textit{Thio} \\
0.30 & & 2.25 \\
0.85 & & 30.40 \\
\hline
0.55 & & 28.15 \\
\hline
0.55 \times 1.044 & = & 0.57 \\
\cline{3-3}
 & & 27.58 \text{ c.c.}
\end{array}
$$

27.58 c.c. N/10 thio $= \frac{27.58}{1000} \times 0.1 \times 126.9$ g. iodine = 0.350 g.

(B) VOLUMETRIC DETERMINATION OF ACIDS AND ALKALIS

One litre of a normal solution of caustic soda contains 40.06 g. sodium hydrate, corresponding to the chemical symbol NaOH.

One litre of a normal solution of hydrochloric acid is neutralized by, or is *equivalent to* one litre of normal caustic soda; it contains 36.46 g. hydrogen chloride, corresponding to the symbol HCl.

One litre of a normal solution of sulphuric acid is neutralized by one litre of normal caustic soda; it contains 49.04 g. absolute sulphuric acid corresponding to $\frac{1}{2}H_2SO_4$.

Comparison of Solutions

Fill the burettes with decinormal hydrochloric acid (right) and approximately decinormal caustic soda (left). Run about 20 c.c. of the acid into a beaker, add a little litmus or phenol phthaleïn solution as indicator, then alkali till the colour changes. Litmus is red in acid and blue in alkaline solution; phenol phthaleïn is colourless in acid and red in alkaline solution. (Note that carbon dioxide, for instance of the breath, spoils the end-point in both cases; the indicator "methyl orange" is not affected by carbon dioxide).

Example:

$$
\begin{array}{lcl}
\textit{Alkali} & & \textit{Acid} \\
0.15 & & 0.65 \\
24.25 & & 24.60 \\
\hline
24.10 \text{ c.c.} & = & 23.95 \text{ c.c.} \\
\hline
1.00 \text{ c.c.} & = & 0.994 \text{ c.c.}
\end{array}
$$

If the acid be 0.1020 normal, what will be the normality of the alkali?

Note—At the end of the exercise the burettes should be refilled with the cleaning mixture of chromic and sulphuric acids, and the pipettes should be left standing in jars of the same mixture.

EXERCISE 2

TO ILLUSTRATE FARADAY'S LAW

In this exercise the current is passed through a solution of zinc iodide, and a solution of caustic soda, in series with a milammeter. By noting the current and the duration of the electrolysis, the number of coulombs that has passed through the solutions is ascertained; the amount of iodine liberated is determined volumetrically; and the amount of hydrogen set free is found from the volume of the gas, its temperature, pressure and composition.

Preliminaries

Determine the polarity of the 110 volt terminals on your switchboard by connecting two wires through a lamp-rheostat to the ends of a piece of moistened litmus paper. (Remember that one of the wires is grounded!)

Saturate the caustic soda solution with gas (why?) by connecting the electrodes for a few minutes to the terminals of the 110 volt circuit through two 8 c.p. carbon lamps in series.

The Electrolysis

Fill the gas measuring tube with water at room temperature, not direct from the tap (why?). Invert it over the end of the delivery tube in the beaker, taking care that no air bubbles get in. (If the beaker be first filled with water, and the tube be then filled from the beaker, there will be no danger of overflowing during electrolysis).

Fill the iodine apparatus with zinc iodide solution and insert the electrodes.[1] The zinc electrode is enclosed in a cotton bag (why)? Connect the two electrolytic cells and the milammeter in series with two 8 c.p. lamps taking care that the platinum electrode is made anode. (Why?)

Note the time and close the circuit. Allow the current to pass for about forty minutes, noting the time closely. Record the ammeter reading every five minutes during the electrolysis, and take the average as the "current." Hence find the number of coulombs pased through the solutions.

During electrolysis fill the burettes with volumetric iodine and thio solutions and "compare" them.

---

[1] *The apparatus should be rinsed with a little of the zinc iodide solution before filling it. The rinsings, the solutions after titration, and all other liquids containing iodine (whether free iodine or iodides) should be poured into the receptacle provided for that purpose, and NOT DOWN THE SINK. When inserting the electrodes, do not put the corks in too tight.*

2

Iodine Determination

At the close of the electrolysis immediately remove the zinc electrode (why?); pour the solution into a beaker, dissolve (in the potassium iodide solution provided) any iodine adhering to the anode (be sure to get it all!) and rinse into the beaker. Then determine the iodine by adding volumetric thiosulphate, etc., as described in Exercise I. When the analysis is completed, pour the contents of the beaker into the receptacle provided for "iodine residues."

Calculate the total weight of iodine liberated during the electrolysis.

Hydrogen Determination

Volume.—Read the volume, C, of the gas, in cubic centimetres; $\frac{2}{3}$C is the volume of (wet) hydrogen liberated. (Why?).

Temperature.—The temperature of the gas may be assumed to be the same as that of the water in contact with it. Determine this in degrees Centigrade (t) with the thermometer.

Pressure.—Note the height of the water column in millimetres, and divide by 13.6 to give the equivalent height of mercury. (Why?). Subtract this from the barometer reading (why?) and from the difference subtract the "vapour tension" of water for the proper temperature as given in the table below. The result gives the "pressure," P, of the dry gas.

The relation between the temperature $T = t + 273$, volume $V = \frac{2}{3}C$, pressure P, and weight of any gas is given by the equation:

$$PV = 62370\ n\ T,$$

$$\text{whence } n = \frac{PV}{62370\ T}$$

where *n* is the number of gram-formula weights of the gas in the volume V c.c. In the case of hydrogen (H^2) each formula weight is 2.016 g., so that 2.016 *n* grams of hydrogen are contained in the C c.c. of electrolytic gas.

Electrochemical Equivalent and Faraday's Constant

From your results calculate (1) the number of coulombs that must be passed through the solution to liberate 1.008 g. hydrogen. (Why 1.008 g.?), and (2) the weight of iodine liberated per 1.008 g. hydrogen set free.

Table of Vapour Tensions of Water

N.B.—The temperature is given in degrees centigrade, the pressure is given in millimetres of mercury.

deg.	*mm.*	*deg.*	*mm.*	*deg.*	*mm.*
10	9.2	15	12.7	20	17.4
11	9.8	16	13.5	21	18.5
12	10.5	17	14.4	22	19.6
13	11.2	18	15.4	23	20.9
14	11.9	19	16.3	24	22.2

2

NOTE ON THE LECTURE EXPERIMENTS

In the lectures accompanying this laboratory course, typical solutions are electrolysed and the products of electrolysis identified by the usual chemical means. The student should tabulate the results there obtained; they will help him guess what the results of electrolysis will be in other cases.

In the lectures, also, the following quantitative measurements are made:

(1) Two solutions of sulphuric acid, of different concentrations, are electrolysed in series. The potential difference over each cell, the volume of hydrogen liberated in each cell, and the volume of oxygen liberated in each cell are measured.

(2) The volumes of hydrogen liberated per minute during electrolysis of a solution of sulphuric acid with two different measured currents are determined.

(3) The acid and alkali formed by electrolysis of a solution of sodium sulphate coloured with red cabbage are mixed.

(4) A solution of sulphuric acid and one of sodium sulphate are electrolysed in series, and the volumes of hydrogen liberated in each are measured.

(5) A solution of potassium nitrate and one of sodium sulphate are electrolysed in series, and the solution from the cathode compartment of the first is mixed with the solution from the anode compartment of the second.

(6) A solution of sulphuric acid and one of sodium sulphate are electrolysed in series, and the weight of hydrogen from the first is compared with the weight of sulphuric acid from the second.

A little thinking over the results of these measurements will give a student a clearer idea of the content of "Faraday's law" and of the meaning of "electrochemical equivalent," than any attempt to memorize a form of words.

EXERCISE 3

SECONDARY REACTIONS

When a solution of sodium chloride is electrolysed in a U-tube with platinum electrodes, so that the substances formed at the two electrodes are kept apart, the final products of the electrolysis are chlorine, hydrogen, and sodium hydrate solution in the quantities represented by the symbols Cl, H, and NaOH for every 96540 coulombs passed through the solution.

If, however, the chlorine and alkali be allowed to mix, they unite to form sodium hypochlorite, NaClO, thus:

$$2\ NaOH + Cl_2 = NaCl + NaClO + H_2O,$$

and this, on standing, is gradually converted into sodium

chlorate, $NaClO_3$, at a rate depending on the temperature and concentration of the solution, according to the equation:

$$3\ NaClO = NaClO_3 + 2\ NaCl.$$

These two reactions are independent of the electric current, and would take place whether there were electrodes in the solution or not; they are consequently spoken of as "secondary reactions."

Thus when a solution of sodium chloride is electrolysed in a beaker, the electrolyte soon contains sodium hypochlorite and sodium chlorate as well as sodium chloride. Now, when a pure solution of sodium hypochlorite is electrolysed, oxygen and chlorate are formed at the anode, and at the cathode hypochlorite is reduced to chloride. The same reactions take place in the presence of sodium chloride; in the beaker therefore, less chlorine and less alkali are liberated per coulomb than in the U tube; some of the current acting on the hypochlorite. Taking the electrochemical equivalent of sodium hypochlorite to be $\frac{1}{2}NaClO$ (why?), and that of sodium chlorate to be $\frac{1}{6}\ NaClO_3$ (why?), the "current efficiency" in the formation of these two substances by the electrolysis of sodium chloride solution is expressed by the quotient:

$$\frac{96540\ (Hy+Chl)}{\text{Coulombs}}$$

(why?) where Hy and Chl denote the number of equivalents of hypochlorite and chlorate produced during the electrolysis.

From what precedes, this "current efficiency" will depend on the temperature, alkalinity, and concentration of the solution electrolysed; it also depends on the nature of the electrodes, and is affected by the addition of small amounts of calcium salts, chromates,[1] etc. (for an explanation see "bandaged electrode" Exercise 9). To illustrate this, the conditions under which the electrolysis is carried out are different for each student; special instructions as to these will be found at each working place, the following apply to all.

Electrolysis

Fill the cell with the solution specified in the special instructions, measuring the volume with a 100 c.c. graduated cylinder. Set the stirrer going. If necessary, heat to the prescribed temperature; then connect in series with an ammeter, lamp-rheostat, and switch, to the 110 volt terminals.

At 30, 60, 90 and 120 minutes after throwing on the current, measure out 5 c.c. of the electrolyte into a beaker with a pipette. *Each of these samples is to be used for the determination of both hypochlorite and chlorate.* The total volume of electrolyte in the cell must be kept constant by adding 5 c.c. of unelectrolysed solution every time a sample is withdrawn for analysis.

---

[1] *Note green precipitate on cathode.*

Volumetric Determination of Hypochlorite

The 5 c.c. sample is diluted in the beaker with water to about 50 c.c. (why?) and volumetric sodium arsenite is added until the hypochlorite is completely reduced. The reaction is expressed by the following equation:

$$NaClO + Na_3AsO_3 \text{ (arsenite)} = NaCl + Na_3AsO_4 \text{ (arsenate)}.$$

In this determination an "external" indicator is used, consisting of filter paper moistened with a solution of potassium iodide containing starch. The arsenite is added very gradually until a drop of the solution in the beaker when transferred on the end of a stirring rod to the starch-iodide paper fails to turn it blue. (Explain.)

One litre of decinormal arsenite reacts with 1/10 equivalent, *i.e.*, 1/20 formula weight, of sodium hypochlorite, $NaClO$. From the volume of sodium arsenite solution needed, calculate the number of equivalents of sodium hypochlorite produced in the cell from the beginning of the electrolysis to the time when each sample was taken out.

Volumetric Determination of Chlorate

For this determination use *the solution in which the hypochlorite has already been determined.* First add a few cubic centimetres of dilute sulphuric acid, then excess of volumetric ferrous sulphate from burette (about 3 c.c. decinormal solution for every 30 ampere-minutes) and heat to boiling. Cool the solution by pouring in more than its own volume of water, and then add volumetric permanganate from second burette until a slight permanent pink coloration remains.

The sodium chlorate oxidizes its equivalent of ferrous sulphate; the permanganate is used to determine the amount remaining unoxidized. Thus (knowing the ratio between the permanganate and the ferrous sulphate) the net amount of ferrous sulphate required for the reduction of chlorate is determined, and hence the quantity of chlorate contained in the sample.

One litre of decinormal ferrous sulphate reacts with 1/10 equivalent, *i.e.*, 1/60 formula weight, of sodium chlorate, $NaClO_3$. (Why six equivalents in one formula weight? Refer to equations at beginning of this exercise).

Calculation

Calculate the total amount (*in equivalents*) of hypochlorite and chlorate produced in the cell during the first 30, 60, 90 and 120 minutes of electrolysis.

Calculate the "current efficiency" as defined above, for each of these periods.

[illegible]

[illegible]

[illegible]

[illegible]

[illegible]

[illegible]

[illegible]

$$[illegible]$$

[illegible]

[illegible]

[illegible]

Plot as ordinates on a time base the following:

1. Equivalents of hypochlorite,
2. Equivalents of chlorate,
3. The sum of these two, or "total oxidation observed,"
4. Total oxidation corresponding to 100% efficiency, viz., coulombs /96540.

These calculations must be made immediately after the completion of each analysis, and the results plotted on the coördinate paper posted on the board. Thus every member of the class can see how the results are being affected by the different conditions under which the electrolyses are being carried out.

Report

Write a brief description of the experiment stating the material of the electrodes, composition and volume of electrolyte, current, current densities at anode and cathode, and temperature.

The record should also contain the volumes of arsenite, ferrous sulphate and permanganate solutions used for each determination.

EXERCISE 4

TRANSPORT OF CHLORINE IN SOLUTIONS OF LITHIUM, SODIUM, AND POTASSIUM CHLORIDES

When 96540 coulombs of electricity are passed through a solution of sodium chloride, chlorine is liberated at the anode and hydrogen and sodium hydrate at the cathode in amounts represented by the chemical symbols Cl, H, and NaOH respectively.

It has been found, moreover, that if the cell be divided into two parts, the total amount of sodium in the cathode compartment is greater after the electrolysis than before it, while the amount of sodium in the anode compartment is correspondingly less. Sodium is therefore spoken of as an "ion" (the cation) and is said to "migrate" or "be transported" from the anode compartment to the cathode compartment during the electrolysis. The amount transported is found to be proportional to the quantity of electricity that has passed through the solution, and *the transport number of sodium*, H_{Na}, *is defined as the number of equivalents* (*or rather the fraction of an equivalent*) *of sodium that passes from the anode compartment to the cathode compartment with* 96540 *coulombs*, i.e., (under the conditions of the present exercise) while one equivalent of sodium hydrate is liberated at the cathode. (Why is the qualification needed?)

For similar reasons chlorine is said to be the "anion" in sodium chloride solutions, and its transport number H_{Cl}, is defined as the number of equivalents of chlorine that pass from the cathode compartment to the anode compartment with 96540 coulombs, i.e., under the conditions of the present exercise, while one equivalent of chlorine is liberated at the anode, or one equivalent of sodium hydrate at the cathode.

The transport number of sodium is not the same in solutions of different sodium salts, it also changes slightly with the concentration and temperature of the solution; the same is true of the transport numbers of other ions.

Since $H_{Na}+H_{Cl}=1$ (why?) both transport numbers may be determined by measuring: (*a*) the gain of sodium in the cathode compartment, or (*b*) the gain of chlorine in the anode compartment, or (*c*) the loss of sodium in the anode compartment, or (*d*) the loss of chlorine in the cathode compartment, while a measured quantity of electricity passes through the solution. Of these (*d*) offers the least experimental difficulty (why?); it is therefore adopted in the following exercise. The amount of electricity passed through the solution is ascertained by determining the quantity of sodium hydrate set free at the cathode.

The Electrolysis

Rinse the "transport cell" with a little of the solution to be used in the exercise and drain it (why?).

Fill the transport cell with an approximately decinormal solution of sodium chloride, taking care that no air-bubbles are left in the rubber tube which connects the two halves of the cell.

Connect the cell in series with a 32 c.p. carbon lamp to the 110 volt terminals, noting the time when the circuit is closed. Allow the electrolysis to continue for 40 minutes.

During the electrolysis determine the "strength" of the sodium chloride solution by volumetric silver nitrate (as described below).

After the electrolysis, immediately clamp the central piece of rubber tube and run the contents of the *cathode compartment* into a 60 c.c. measuring flask. The solution will not quite fill the flask to the 60 c.c. mark, so pipette a few c.c. of the original (stock) sodium chloride solution into the cathode compartment, washing down by this means any sodium hydrate which may be left adhering to the electrode, and add these washings carefully to the contents of the flask until the 60 c.c. mark is reached. Mix the contents of the flask by shaking.[1]

---

[1] *While performing this operation, the student should reflect that one of his next steps is to determine the amount of chlorine in the very solution to which he has just added an unknown, but far from negligible, amount of sodium chloride; and that the "transport number" he finally obtains depends on the result of this chlorine determination. The man who thinks out* for himself *how these things can be, will have no trouble with transport numbers.*

Determination of the Quantity of Electricity

Rinse a clean burette with a few c.c. of this "cathode solution," let drain, and then pour in the rest of the solution. Note the reading of the burette, then run about 20 to 25 c.c. of the solution into a beaker. Add a few drops of phenolphthaleïn solution, and then N/20 sulphuric acid (from another burette) until the coloration disappears. *Keep this neutral solution for the determination of its chlorine content.*

From the titration calculate the number of equivalents of sodium hydrate (NaOH) in the 60 c.c. of cathode solution, and from this the number of coulombs passed during the electrolysis.

NOTE.—For the purpose of obtaining the transport number in this exercise it is not necessary to calculate the number of coulombs. (Why?).

Determination of Chlorine in the Cathode Solution

To the neutral solution in the beaker add two or three drops of a saturated solution of potassium chromate, and determine the chlorine by means of decinormal silver nitrate, as described below. The original (stock) sodium chloride solution should be used for "titrating back."

NOTE.—In making the determinations of sodium hydrate and chlorine, it is convenient to have four burettes arranged in the following order: cathode solution, volumetric sulphuric acid, volumetric silver nitrate, and stock sodium chloride solution. Why is it more convenient to have the cathode solution in a burette, than to leave it in the flask and pipette some out for analysis?

Calculation of the Transport Numbers

The difference between the number of equivalents of chlorine in the 60 c.c. of "cathode solution" and the number of equivalents in 60 c.c. of the original (stock) sodium chloride solution is evidently (?) the loss of chlorine from the cathode compartment. The number of equivalents of sodium hydrate liberated during the same electrolysis is also known (first titration). From these two data, and the definitions on page 13, the "transport numbers" may be calculated.

NOTE.—THE VOLUMETRIC DETERMINATION OF CHLORINE IN CHLORIDES.

Chlorine in chlorides may be determined by means of a volumetric solution of silver nitrate, using a cold saturated solution of potassium chromate as indicator. On dropping the volumetric silver nitrate into a *neutral* solution containing a soluble chloride and two or three drops of the indicator, a mixture of (white) silver chloride and (red) silver chromate is precipitated; on stirring, however, the silver chromate is decomposed by the soluble chloride remaining in the solution, and it is only when all of the latter has been decomposed that the precipitate retains permanently a reddish colour; this is taken as the end point.

The relation between the quantity of sodium chloride in the solution and the quantity of silver nitrate required in the titration is given by the equation:

$$AgNO_3 + NaCl = AgCl + NaNO_3.$$

NOTE.—RELATION BETWEEN THE TWO TRANSPORT NUMBERS.

The relation $H_{Cl} + H_{Na} = 1$ is explained and illustrated in the lectures accompanying this laboratory course; any difficulty the student may have met should be removed by thinking over the results of his own measurement.

If, for example, in his electrolysis, the cathode compartment lost 0.000615 equiv. chlorine, while 0.001015 equiv. sodium hydrate were formed, how many equivalents of sodium must the cathode compartment have gained? Evidently $0.001015 - 0.000615 = 0.00040$; this is the step that needs to be thoroughly understood. It follows immediately that for every 96540 coulombs passed through the solution, 0.000615/0.001015 equiv. chlorine has left the cathode compartment, and 0.00040/0.001015 equiv. sodium has entered it. These fractions are the "transport numbers" of chlorine and sodium respectively, as determined from his measurements; that they must add up to unity is obvious from the way the second was calculated from the first.

EXERCISE 5

DETERMINATION OF THE CONDUCTIVITY OF ELECTROLYTES

It may be shown by considerations based on Ohm's law, that in an arrangement of conductors such as that represented in Fig. 1, no current will flow through *T* if the resistance of *A* stands to that of *B* as the resistance of *C* does to that of *D*.

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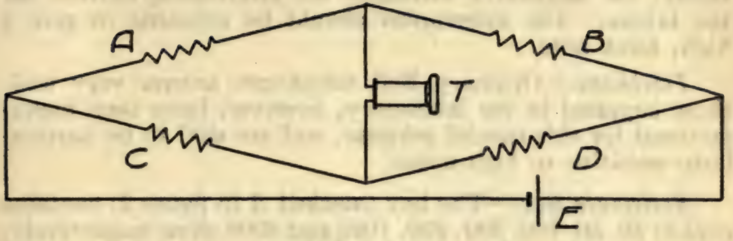

FIG. 1

Wheatstone Bridge

The Wheatstone Bridge is an arrangement for measuring resistance based on this relation; the unknown conductor takes the place of B in the diagram, and the resistances C and D are varied until no current can be detected in T, when the resistance B may be found from the proportion $A : B :: C : D$, or $B = AD/C$; and the conductivity, $1/B = C/AD$.

When measuring the conductance of metals or other conductors of the first class, direct current is generally employed, and a galvanometer is placed in the circuit T; in the case of electrolytes, however, the passage of the current would decompose the solution whose resistance was being measured, and might also introduce an e.m.f. (polarization) into B, thus interfering with the accuracy of the measurements. Alternating current is consequently employed, and a telephone is used as detector in T. Fig. 2 shows everything ready for use; the letters A, B, C, D, T, indicating the positions occupied by the various pieces of apparatus in the scheme of diagram 1.

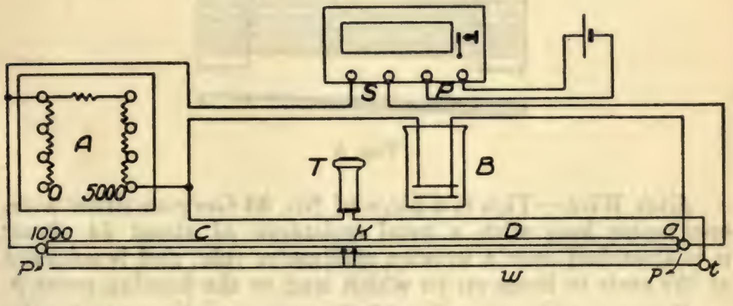

FIG. 2

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Induction Coil.—The primary circuit is supplied with current from two cells of the storage battery in series (four volts); the secondary furnishes the alternating current for the bridge. The interruptor should be adjusted to give a high, faint note.

Telephone.—Ordinary Bell telephones answer very well; those supplied in the laboratory, however, have been manufactured for this special purpose, and are said to be particularly sensitive to high notes.

Resistance Box.—The box (marked *A* in figure 2) contains coils of 50, 50, 100, 300, 500, 1000 and 3000 ohms respectively, joined in series. The number at each post gives the total resistance in ohms measured from the post marked 0.

In order to minimize self-induction and capacity, either of which would interfere with the truth of the equation above obtained, a special construction shown in Fig. 3 has been employed. A flat wooden frame has been used for each coil and by means of a winding rule involving sometimes straight and sometimes diagonal crossings between the sides, it has been arranged that along some lines every alternate wire, along others every alternate pair shall carry currents in opposite senses thus minimizing self-induction, while as in the Chaperon winding minimum capacity is obtained by the wide separation of the ends.

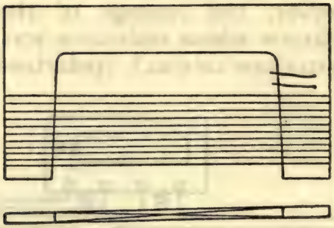

Fig. 3

Slide Wire.—This is a piece of No. 33 German silver wire, one metre long with a total resistance of about 14 ohms; it is stretched over a wooden millimetre rule, and is soldered at the ends to brass strips which lead to the binding posts *p*.

Contact with any point of the wire may be made by the *sliding contact K*, which is connected to one of the terminals of the telephone by way of the fixed copper wire *w* and the binding post *t*; the part of the wire to the left of the contact then takes the place of *C* in Fig. 1, and that to the right of the contact corresponds to *D*; so that if contact be made at the point 513 mm., and if it be assumed that the wire has uniform resistance throughout, $C/D = 487/513$.

The slider is provided with two contacts, either of which may be used alone, the slider being moved until no sound is heard in the telephone. But in some cases, especially when the resistance measured is high, the position corresponding to the minimum of sound is uncertain, and a decision may be best arrived at by pressing the two contacts alternately, and moving the slider until both give the same sound; the reading must be taken midway between the two contacts.

In using the bridge, the resistance box *A* should be adjusted so that, when no sound is heard in the telephone, the contact is near the centre of the wire; as an error of one millimeter at the point 500 introduces an error of only 0.4% in the ratio C/D, while at the point 800 (or 200) for instance the error is 0.6%, and at 900 (or 100) it reaches 1.1%. (The student should verify this).

Calibration of the Slide Wire.—Before any but the roughest measurements, the bridge wire must be calibrated. Ten approximately equal resistances of German silver wire are prepared (their total resistance being about the same as that of the bridge wire) by soldering to the ends of equal lengths of suitable wire short pieces of stout copper wire which are afterwards amalgamated. Eleven holes are bored into, but not through, a strip of wood, which is then laid down parallel to the bridge wire, the holes are filled with mercury and the ten resistances arranged in them as shown in Fig. 4. The two wires from the induction coil are connected to the binding posts *p*, which are joined by heavy copper leads to mercury cups No. 1 and No. 11; the telephone is connected with cup No. 2 and the post *t*; and the point is found at which the telephone is silent. Now the first resistance *r*, which is provided with some mark to distinguish it from the others, is made to change places with the second; the position of the contact is then determined when the telephone is connected with cup No. 2 and again when it is connected with No. 3, the difference of the readings being noted. The resistance *r* is then brought between cups 3 and 4, and the process repeated, until *r* comes finally between 10 and 11, at which place only one reading, with the telephone wire in 10 is needed. By these measurements ten portions of the bridge wire of equal resistance have been determined, each portion being approximately one-tenth of the whole.

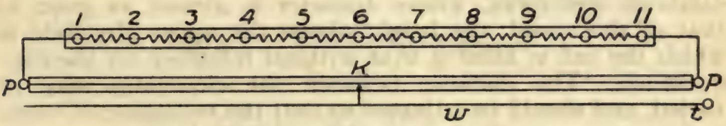

FIG. 4

The ten differences are added up, and the difference between the sum and 1000 mm. divided by ten; each separate value must then be corrected by the amount thus obtained, so that the sum is now exactly 1000 mm. If the single corrected lengths are now added, thus 1, 1+2, 1+2+3. . . . they give the points which correspond to successive tenths of the resistance of the wire; and the differences between these numbers and 100, 200, 300 . . . mm. are the corrections to be applied at the corresponding places. For example, if the sum of the first three lengths is 298.7 mm., to each reading in the neighbourhood of 300 mm. the correction 1.3 must be added.

Thermostat

As the conductivity of most electrolytes increases several percent for every degree rise of temperature, the flasks containing the solutions to be measured should be kept in an ice bath, in a current of tap water, or in the water of a self-regulating thermostat, until the solutions have attained the temperature of the bath, before they are transferred to the conductivity vessel. The latter should also be kept in the bath, both during the measurement and for some minutes before it.

If it should be necessary in order to get a good minimum of sound, the electrostatic capacity of the vessel may be lessened by immersing it in a beaker of coal-oil standing in the thermostat.

Conductivity Vessel

This is a cylindrical glass vessel, provided with two circular platinum electrodes, whose diameter is almost as great as that of the vessel; the height above the upper electrode to which the cell is filled is thus without influence on the conductance. The distance between the electrodes may be varied, and should be adjusted so that the resistance of vessel and contents may lie between 50 and 2000 ohms.

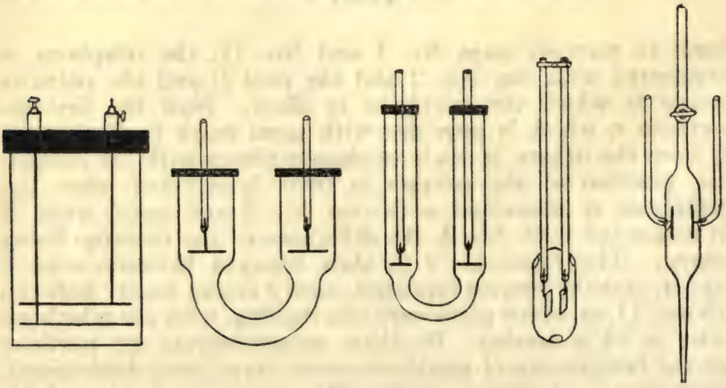

Fig. 5

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Some of the commoner forms of conductivity vessel are shown in Fig. 5. At the left of the figure is the cell just described, then a form adapted for good conducting liquids, one for small quantities, a "dip electrode"[1] for measuring the conductivity of liquids in beakers or bottles, and a "pipette electrode" for volatile liquids, or for liquids in narrow-necked vessels. In all but the first, contact with the electrodes is made through mercury contained in the glass tubes into which they are sealed; in handling them, care should be taken not to spill this mercury.

Platinizing the Electrodes.—The electrodes are covered with a layer of platinum black by electrolysis; this helps to prevent polarization, and when the platinizing has been well done very small electrodes may be employed. The electrolyte used for this purpose consists of 3 g. of platinum chloride, and 0.025 g. of lead acetate dissolved in 100 c.c. of water. The current should be about 0.15 amperes for each square centimetre of (one side of) the electrode; it should be passed for about fifteen minutes, during which its direction is changed four or five times. After platinizing, the electrodes must be thoroughly washed, and soaked in repeated changes of water for some hours before use; the last traces of the platinizing solution being got rid of by joining the electrodes to the secondary terminals of the induction coil, and letting them stand in the conductivity vessel, filled with water. The deposit of platinum black is easily rubbed off, it must not be touched with the fingers.

Calibration of the Conductivity Vessel.—The necessity of determining the dimensions of the vessel, and the distance between the electrodes, may be obviated by determining its conductance when filled with some solution whose specific conductivity is known. Full data for those in common use are given in Tables IV, V. For example: the specific conductivity of tenth-normal potassium chloride at 7°C is 0.00866 (Table IV); if then the conductance of the vessel when filled with this solution is found to be 0.01704 reciprocal ohms (mhos) at 7° C, the specific conductivity of any other electrolyte may be found by determining its conductance in the same vessel, and multiplying by 0.00866/0.01704. This fraction is called the "factor" of the vessel.

Conductivity Water.—A determination of the specific conductivity of water from one of the taps in the laboratory gave 110×10^{-6} at 0° C; distilled water from an "automatic still" 55×10^{-6}, and distilled water from a chemical wash bottle 12×10^{-6}. None of these samples of water would serve for the measurements described below.

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[1] *Why are the electrodes in the "dip electrode" surrounded by a glass bulb? Would the reading be different if the bulb were omitted?*

The "conductivity water" supplied in the laboratory is prepared from distilled water, by first boiling it to expel carbonic acid, and then distilling it with potassium permanganate and sulphuric acid, passing the steam through a boiling solution of potassium permanganate and caustic potash, and condensing it in a block tin condenser. The water is collected in Jena glass flasks, which are previously well boiled out. Its specific conductivity at 0° C is about 1.5 to 2×10^{-6}; on long standing, however, it dissolves the glass, and its conductivity rises. Care must be taken to protect it from the carbon dioxide of the breath, and of flames; on blowing through a sample for half a minute, its specific conductivity rose from 1.8×10^{-6} at 0° C to 6×10^{-6}.

TO MAKE A SERIES OF MEASUREMENTS OF THE CONDUCTIVITIES OF SOLUTIONS OF THE SAME SUBSTANCE BUT OF DIFFERENT CONCENTRATIONS.

Place the conductivity vessel, and flasks containing the solution to be measured, the calibration solution, and the conductivity water, in the thermostat.

Set up the apparatus as shown in Fig. 2. The resistance of the wires supplied for connections may be neglected in comparison with those of the box and of the solutions.

See that the solutions have attained the temperature of the bath.

Pour about 30 c.c. of the calibration solution into the conductivity vessel, taking care that no air bubbles remain on the under surface of the upper electrode. (Why not measure accurately?)

Connect the induction coil with the battery, and adjust the interruptor.

Determine the conductance, adjusting the resistance box so that the reading may be as close as possible to the middle of the wire.

Read again after a minute or two. If the temperature of the solution has risen the conductance will have increased, and *vice versa*. The readings must be repeated until constant results are obtained.

[If the electrodes have recently been platinized, the calibration solution should now be poured out, and replaced by a fresh portion; and the conductance should be determined again, to make sure that the electrodes have been properly cleaned.]

From the final reading, and the data of Table IV, calculate the "factor" of the vessel. Pour out the calibration solution, rinse the vessel with water, dry it, and let it stand in the thermostat a minute or two. The surfaces of the electrodes

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must not be touched or the platinum black will rub off; the water may be removed from them by touching the edge with a piece of filter paper.

Pipette in 30 c.c. of the solution whose conductivity is to be determined. Touch the side of the vessel with the point of the pipette, and let it drain for 15 seconds, but do not blow into it. (Why must this volume be measured accurately?)

Determine the conductance as before, and multiply by the factor of the vessel, thus obtaining the specific conductivity of the solution.

Remove 15 c.c. of the solution from the conductivity vessel with a pipette, and replace it by 15 c.c. of the conductivity water. Mix by moving the electrodes gently up and down, and determine the specific conductivity.

Repeat, until the resistance of the vessel rises to about 10,000 ohms; always keeping one of the pipettes for adding the water, and the other for removing the solution, and being careful not to blow into them. Unless the temperature at which the measurements are being made is within a few degrees of that of the room, the pipettes should be kept in tubes standing in the bath.

Finally, set the electrodes about 5 mm. apart, and determine the conductance of the "conductivity water;" then recalibrate the vessel with fiftieth normal potasssium chloride, and calculate the specific conductivity of the water. This must be subtracted from the specific conductivities previously determined. *Note:* If the conductivity of the water is to be used for this purpose only, it need not be known very accurately; and instead of recalibrating the cell, it will be sufficient to measure the distance between the electrodes with the metre stick of the slide wire, before and after moving them.

Report.—The report should contain a sketch of the apparatus. The numerical data should be arranged in columns; the first, under ϕ, giving, in cubic centimetres, the volume of the solution that contains one equivalent of the dissolved substance; the second, the resistance in the box; the third, the reading on the wire; the fourth, under κ, the specific conductivity; and the fifth, under $\Lambda = \kappa\phi$, the equivalent conductivity.

The last few numbers may have to be corrected for the conductivity of the water; the corrected number might be written under the other, and marked "corr."

TO DETERMINE THE SOLUBILITY OF LEAD SULPHATE BY MEASURING THE CONDUCTIVITY OF ITS SATURATED SOLUTION.

Precipitate the lead sulphate, in a test tube, from a hot solution of lead acetate with dilute sulphuric acid; filter, and wash well with distilled water. Then make a hole in the paper, wash the precipitate through it into the conductivity vessel, and determine the conductance.

Pour off the liquid, replace it by fresh conductivity water, and determine the conductance again; repeating this operation until a constant number is obtained. (Why?) Then calculate the specific conductivity, which, after subtracting that of the water, may be regarded as the specific conductivity of the saturated solution of lead sulphate.

By means of the following table of the equivalent conductivity of lead sulphate solution computed from the mobilities (how?) calculate the solubility of the lead sulphate, (*a*) in equivalents per litre, (*b*) in grammes per litre. $PbSO_4 = 302.96$ g.

Equivalent Conductivity of Lead Sulphate Solutions.

t	Λ_∞	t	Λ_∞
0° C	75.6	15° C	113.2
5	87.5	20	126.8
10	100.0	25	141.1

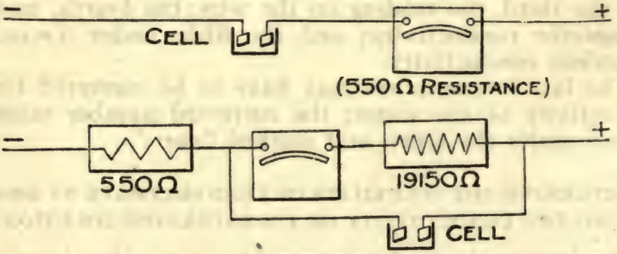
EXERCISE 6

DECOMPOSITION VOLTAGES

The Apparatus

In this exercise a voltage is "tapped off" from a double-slide rheostat[1] connected to the 4-volt terminals of the storage battery. From this tapped-off voltage a circuit is drawn through a triple-pole double-throw switch in such a manner that the microammeter may be used to read the *voltage* across the cell when the switch is put down on one side, and the *current* flowing through the cell when it is thrown to the other side.

The following diagrams, figs. 1 and 2, indicate the circuits when the switch is in the first and second positions respectively:



FIGS. 1 AND 2

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[1] *This is a standard piece of laboratory equipment; in the present exercise no use is made of the coarse wire (low resistance) side.*

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The next diagram, fig. 3, shows the connections as actually used in the exercise:

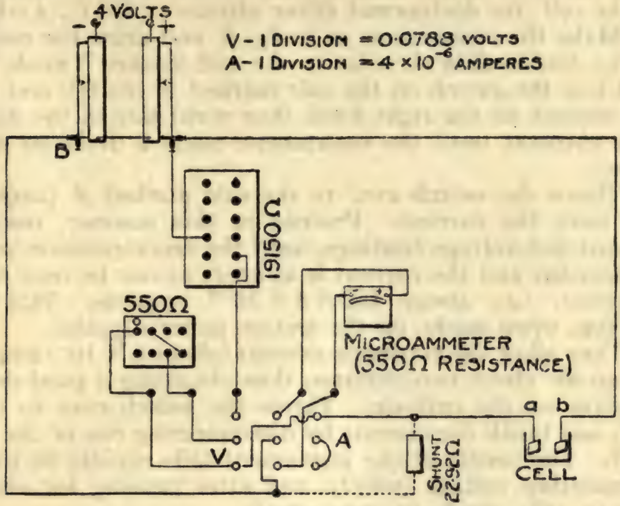


Fig. 3

Note.—The diagrams are lettered for a microammeter of resistance 550 ohms; the instruments used in the laboratory vary from 450 to 560 ohms. The box marked "550Ω" in the diagram must have the same resistance as the microammeter employed, the "shunt" resistance also depends on that of the instrument; the resistance of 19150Ω, being a piece of standard laboratory apparatus, is the same for all. In consequence, one scale division of the instrument when used as an ammeter always corresponds to 4×10^{-6} amperes, but when used as a voltmeter the factor depends on the resistance of the microammeter employed.

Principle of the method.—By means of the double-slide rheostat successive small voltages are applied over the cell (at *a*, *b*) and in each case, the resulting current is noted. So long as the potential difference applied is below the "decomposition voltage," the instrument shows small currents rapidly dropping to zero. When the decomposition voltage is reached the current remains constant, and a further small increase of the applied voltage causes a large increase in the current. If the readings be plotted on a voltage base with currents as ordinates, the curve will show an abrupt change in its slope at the decomposition voltage.

Details of the measurements

First clean the platinum electrodes by dipping in strong nitric acid and rinsing in distilled water.

Silver nitrate.—Put about 10 c.c. of silver nitrate solution into the cell, and adjust the electrodes until they are completely immersed, parallel, and about half an inch apart. (The student should make a rough estimate of the resistance of the cell; for decinormal silver nitrate at 18° C, $\Lambda = 95$).

Make the connections as in fig. 3, and draw the contacts of the double-slide rheostat to the end marked "weak."

Close the switch on the side marked *V* (volts), and move the contact on the right hand (fine wire) side of the double-slide rheostat until the instrument reads 2 divisions of the scale.

Throw the switch over to the side marked *A* (amperes), and note the current. Proceed in this manner, recording current and voltage readings, until the decomposition voltage is exceeded and the current is as great as can be read on the ammeter, *i.e.*, about $150 \times 4 \times 10^{-6}$ amperes. Plot each reading, when made, on the section paper supplied.

Then allow the maximum current (about 6×10^{-4} amperes) to run for about two minutes, thus obtaining a good deposit of silver on the cathode. Throw the switch over to the *V* side, and break the current by disconnecting one of the wires at *B*. The needle of the instrument falls rapidly to the decomposition voltage (why?), and after pausing for about a minute, falls slowly to zero (why?).

Copper nitrate.—Clean the electrodes with acid, rinse, and repeat the measurement with copper nitrate solution in the same cell. Plot the readings to the same scale as before.

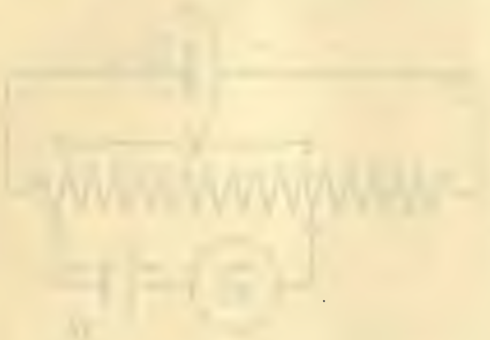
Silver and copper nitrates.—Clean the electrodes, rinse. Place a mixture of equal parts of silver nitrate and copper nitrate solutions in the cell. Leaving the connections as before, proceed to find the first decomposition voltage. Then attach the shunt as indicated by the dotted lines in fig. 3, and replace the 550Ω box by the "balance resistance" of 22 ohms; one division of the instrument will then correspond to 1×10^{-4} amperes (verify this). Proceed as before, noting currents and voltages, until the current is as great as can be read on the ammeter. Plot the readings as before, but use a different scale.

During the latter part of this measurement, after the first decomposition voltage for the mixture has been reached, the electrodes should be cleansed and rinsed between each reading (why?).

EXERCISE 7

MEASUREMENT OF ELECTROMOTIVE FORCE

The e.m.f. of a dry cell or of a storage battery can be read off directly on a "voltmeter," which is an instrument whose reading is proportional to the current obtained by closing the cell through a coil of high resistance included in



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the instrument This method can be used, however, only when (1) the resistance of the cell is negligible in comparison with that of the voltmeter, and when (2) the chemical or other changes in the cell, occasioned by the current needed to operate the voltmeter, do not affect its e.m.f. Neither of these conditions is fulfilled by the small cells used in the following exercise; a method free from these restrictions must therefore be employed.

The electromotive forces are to be measured by a modification of Poggendorff's method (Fig. 1), in which the unknown e.m.f. X is set up in series with a galvanometer G, and opposed to a variable e.m.f. V which is obtained from a cell C of known voltage. The e.m.f. V is then altered until no current flows through the galvanometer.

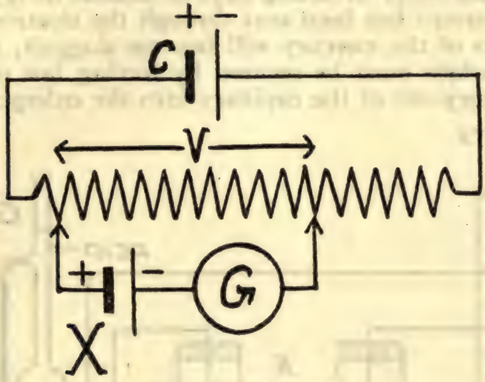

FIG. 1

In the apparatus provided for the following exercise, the galvanometer G is replaced by a capillary electrometer; and instead of providing each student with a cell of known voltage C, a potential difference of 2.00 volts is maintained at each terminal board, by the use of storage battery and rheostats set up in front of the main switchboard where they can be (and ought to be) inspected. The internal resistance of this circuit is negligible. The variable potential difference V is obtained by tapping from a circuit of nine 100-ohm coils and ten 10-ohm coils in series, it can thus be changed only in steps of 0.02 volt, and the scale readings of the electrometer are used to obtain intermediate readings.

The Capillary Electrometer.—The essential feature of this instrument is a contact between mercury and 30% sulphuric acid in a capillary tube; one terminal is in metallic contact with the mercury of the capillary, and the other with a large drop of mercury lying below the acid in an enlargement of the tube. When a potential difference is applied to the terminals, the column of mercury moves up or down in the capillary tube, the direction and extent of the motion depending on direction and magnitude of the e.m.f. applied. The position of the meniscus at the contact between mercury and acid is observed through a small telescope provided with a scale; one scale division corresponds to about 1.5×10^{-8} amperes, which is not far from the delicacy of a good wall galvanometer. Pure mercury and a clean capillary are absolutely essential.

To keep the electrometer in good working order, it must be kept short-circuited except when actually in use; this is accomplished by means of suitable keys, as indicated in Fig. 2, which gives a diagrammatic view of the whole apparatus set up ready for the e.m.f. determination. If this precaution has been neglected (for instance by allowing the contact points of the short-circuiting keys to become dirty), or if too heavy a current has been sent through the electrometer, the movements of the mercury will become sluggish, and a new contact surface must be secured by forcing (air pressure) a little mercury out of the capillary into the enlargement.

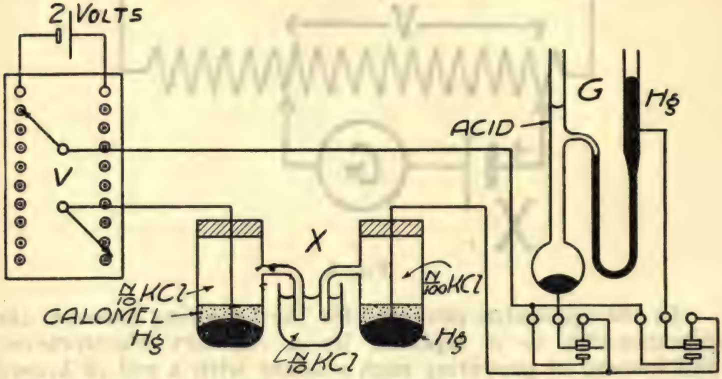

FIG. 2

E.M.F. and Concentration

(1) Set up the cell Hg/HgCl/$\frac{N}{10}$KCl/$\frac{N}{100}$KCl/HgCl/Hg, and measure its e.m.f., noting which electrode is positive.

To set up the cell.—First adjust the corks on the contact tubes, so that the platinum tips will come just to the bottoms of the half cells, being careful not to spill mercury out of the tubes.

Then pour enough mercury into each half cell to fill the rounded bottom.

Next take a little calomel, HgCl, on the tip of a knife and moisten it with the N/10 KCl provided; this is best done by rubbing the calomel with a drop or two of the solution on a sheet of glass; it may then be washed into the half

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cell by a jet of the solution from a pipette. Unless all the calomel be thoroughly wetted, contact between mercury and platinum may be interrupted by dry calomel and air.

Now fill the half cell with its solution, closing the side tube with a finger. Insert the cork, allowing excess solution to escape through the side tube, and see to it that no air bubble remains in the latter (why?).

Finally prepare N/100 KCl (by diluting the N/10 KCl), and set up the second half cell like the first, moistening the calomel with its own solution.

All these manipulations involving mercury and calomel must be carried out over the tray provided; and special care must be taken to prevent either of these substances getting into the sink. Read the General Regulations on "Care of Sinks", and use the receptacle provided.

(2) Replace the $\frac{N}{100}$ KCl by $\frac{N}{1000}$ KCl (prepared by diluting the former) and measure the e.m.f. of the new combination. Compare it with the e.m.f. of No. (1).

What changes take place in these cells during the passage of current? (see note below). Which pole would you have expected to be positive? Why?

Volta's Law

(3) Replace the half-cell containing thousandth normal potassium chloride by a similar half-cell containing a zinc electrode in decinormal zinc sulphate, and measure the e.m.f. of the resulting combination:

$$Hg/HgCl/\frac{N}{10}\,KCl/\frac{N}{10}\,ZnSO_4/Zn.$$

Note which is the positive terminal.

(4) Similarly set up and measure the e.m.f. of the cell: $Hg/HgCl/\frac{N}{10}\,KCl/\frac{N}{10}\,CuSO_4/Cu$.

(5) and of the cell: $Zn/\frac{N}{10}\,ZnSO_4/\frac{N}{10}\,CuSO_4/Cu$.

What relation do you find between the e.m.fs. (3), (4), and (5)?

The combination $Hg/HgCl/\frac{N}{10}\,KCl$, is known as the "tenth-normal calomel electrode." It may be replaced by the "tenth-normal hydrogen electrode" (H_2, Pt/0.1N HCl); in that case the values of (3) and (4) would of course be different from those found above. Would the same relation still exist between the e.m.fs. (3), (4), and (5)?

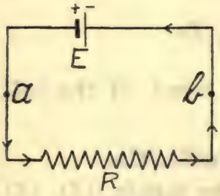
NOTE ON THE E.M.F. OF CONCENTRATION CELLS

In the lectures accompanying this laboratory course, measurements are made of the e.m.f. of cells of the type $Ag/AgNO_3$ conc. $/AgNO_3$ dil.$/Ag$. At the anode in such cells silver dissolves, and at the cathode it is deposited; at the junction of the two solutions, silver passes out of the anode solution into the cathode solution, and nitrate in the opposite direction. The cathode solution thus loses one equivalent of silver by deposition and gains H_{Ag} equivalents by migration per 96540 coulombs; a net loss of $1-H_{Ag}=0.53$ equivalent (see Table III electrochemical data) of silver, or $0.53\times(107.93+14.04+48.00)$ grams of silver nitrate, per 96540 coulombs; and the anode solution gains an equal amount. If the cell be closed, which of the two solutions (concentrated or dilute) will most likely be the anode solution? Which of the two pieces of silver will be the positive pole of the cell?

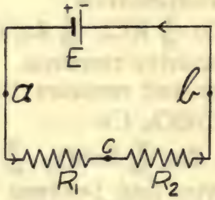
In the cell first measured in this exercise, calomel (HgCl, mercurous chloride) is formed at the anode, and mercury at the cathode (what else?). The anion of the solutions is chlorine, and practically speaking the only cation is potassium; calomel being so insoluble that the amount of mercury in the solution may be neglected. The answer to the question, "which pole would you have expected to be positive" should be worked out by each student for himself.

NOTE ON CURRENT DISTRIBUTION IN NETWORKS

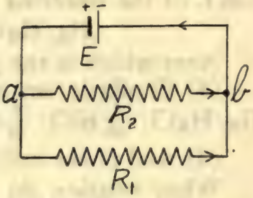
Students unfamiliar with electrical circuits should study the following examples; in all of them it is assumed that the resistances of the cells and of the connecting wires are negligibly small. In general the problem is:—Given e.m.fs. and resistances in the circuits, to find the current through each branch.



(i)



(ii)



(iii)

(i) *One cell and one resistance,*—the simplest case. Circuit (i) consists of a cell of e.m.f. E volts in series with a resistance of R ohms. The direction of the current is fixed by the direction of the e.m.f.; if the + and − signs in the figure be interchanged, the direction of the arrow must be reversed. The magnitude of the current may be found by the following method, which is too cumbersome for such a simple case, but may serve as a type for the others: The points *a* and *b* are the terminals of the cell, and the potential difference between them is E volts, the e.m.f. of the cell, the point *a* being positive with respect to *b*. This may be written $a, b=\mathrm{E}$, naming the positive point first, or $b, a=-\mathrm{E}$. The same points *a* and *b* are also the terminals of a conductor of resistance R ohms, which is carrying the current I amperes from *a* to *b*;

7

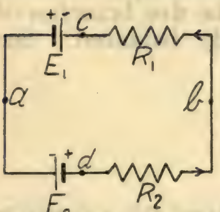
the potential difference (volts) over the ends of such a conductor is given by the product of current (amperes) into resistance (ohms), and is often spoken of as "the I-R drop"; thus (naming the point *from which the current flows* first) $a, b = IR$. Equating these two values for the same potential difference a, b there results $E = IR$ (Ohm's law), and I may be found if E and R are known.

(ii) *One cell and two resistances in series.*—In this case $a, c = IR_1$, $c, b = IR_2$, $a, b = E$; but $a, b = a, c + c, b$; therefore $I = E/(R_1 + R_2)$.

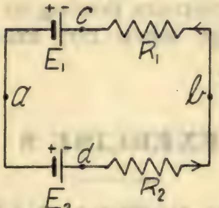
Ex.—If the cell in fig. (ii) have the internal resistance $R_1 = 500$ ohms, (thus the point a is not accessible) and if $R_2 = 400$ ohms be the resistance of a "low reading" voltmeter; what will be the e.m.f. of the cell if the voltmeter reads 0.44 volts?

(iii) *One cell and two resistances in parallel.*—Here $a, b = E$; $a, b = I_1R_1$; $a, b = I_2R_2$. Hence $I_1 = E/R_1$, and $I_2 = E/R_2$.

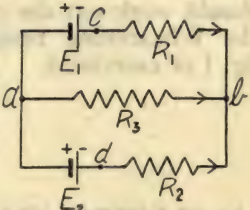
Ex.—If the cell in fig. (ii) be replaced by the terminals of the 110 volt circuit, and the two resistances R_1 and R_2 be each 1000 ohms; what will be the potential difference a, c? What c, b? Will the potential difference a, b be the sum of a, c and c, b? What will be the reading of a voltmeter connected to a and c? to c and b? to a and b? (i) if the resistance of the voltmeter be 2000 ohms, (ii) if it be 20,000 ohms?



(iv)



(v)



(vi)

(iv) *Two cells in series.*—$a, c = E_1$, $c, b = -IR_1$, hence $a, b = E_1 - IR_1$; $a, d = -E_2$; $d, b = IR_2$, hence $a, b = -E_2 + IR_2$. Equating these two values of a, b there follows: $I = (E_1 + E_2)/(R_1 + R_2)$.

(v) *Two cells opposed.*—The potential differences are the same as in (iv) except that $a, d = E_2$ instead of $-E_2$. Hence $I = (E_1 - E_2)/(R_1 + R_2)$ and the direction will be that of the arrow if E_1 be greater than E_2, otherwise opposite.

(vi) *A simple network.*—This circuit occurs in many electrochemical processes, *e.g.*, in electro-refining of metals, in electrolysis with intermediate electrodes, in electroplating ("throw"), etc.; it should be mastered *before* these matters are taken up in the lectures. Assuming E_1. E_2. R_1, R_2, R_3 to be known, the problem is to find magnitude and direction of the current in each branch of the circuit.

Let I_1, I_2, I_3 be the number of amperes flowing *in the direction of the arrow* in each branch; these are the unknowns to be determined. If the value of one of them, say of I_1, prove to be *negative*, this would mean that the current flows through R_1 in the direction opposite to that of the arrow. The current through R_3 must flow in the direction of its arrow (why?); at least one of the other two must flow in the direction opposite to its arrow (why?). When this is understood, it will be clear that $I_1+I_2+I_3=0$.

The other two equations needed to find the three unknowns may be obtained by noting that the (unknown) potential difference $a,b=E_1+I_1R_1$ (from consideration of branch 1), and that it is also equal to $E_2+I_2R_2$ and to I_3R_3. Hence $E_1=I_3R_3-I_1R_1$, and $E_2=I_3R_3-I_2R_2$.

Ex.—Redraw fig. 1 of exercise 7 to make it look like (vi) above.

Ex.—Redraw fig. 3 of exercise 6, with switch thrown for measurement of current, to make it look like (vi) above.

Ex.—If $E_1=110$ volts (switchboard terminals), $E_2=2$ volts (storage cell), $R_1=R_2=R_3=20$ ohms; will the storage cell be charging or discharging? What relation between R_1 and R_3 will result in no current passing through the storage cell in either direction? Does this relation depend on the value of R_2?

(vii) *Wheatstone bridge.*—As a further exercise, the student should work out the currents flowing in the five branches of the Wheatstone bridge when not exactly balanced. See fig. 1 of exercise 5.

EXERCISE 8

(A) ELECTROLYTIC DETERMINATION OF COPPER IN BRASS

Clean the cathode by dipping successively in acid dip, water, and methyl alcohol, shaking the excess of water from the cathode before dipping in the alcohol. Dry over a 32 c.p. lamp (why?), weigh accurately when cool and adjust in the apparatus supplied.[1]

Clean the cell, pipette into it 50 c.c. of the brass solution,[2] add 15 c.c. of a saturated sodium nitrate solution, and dilute

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[1] *A complete description of the King Apparatus may be found in "Chemical and Metallurgical Engineering" Vol. 21, 25-9 (1919).*

The magnetic stirring apparatus is described in "Quantitative Analysis by Electrolysis", Classen-Hall, 5th edition, p. 70. and in

The Journal of the American Chemical Society Vol. 29, 1596 (1907).

[2] *The brass solution is prepared by dissolving 10.000 grams of brass in about 200 c.c. of a solution of mixed nitric and sulphuric acids in water (1:1:5) boiling the solution till the nitric acid is removed, cooling and diluting to one litre. The portion taken for analysis thus corresponds to 0.5000 g. of brass.*

with water until the cathode is well covered. Begin electrolysis with the maximum current specified for the apparatus, and note the voltage over the cell. Why is the solution stirred during electrolysis?

After electrolysing for 40 minutes transfer two or three drops of the electrolyte to a test tube (by means of a pipette) and add to it 2 or 3 c.c. of hydrogen sulphide water. If a brown coloration developes in the test tube, continue the electrolysis for another ten minutes and test again. When no coloration developes, all the copper may be regarded as removed from the solution. Why does not the zinc plate out also?

Remove the cathode from the cell in the manner prescribed for each apparatus, rinse in distilled water, then in methyl alcohol; dry, cool and weigh as before.

Calculate the percentage of copper in the brass.

(B) COPPER COULOMETER (VOLTAMETER)

Dip the smaller spiral in nitric acid, then in distilled water, then in alcohol, and dry over a 32 c.p. lamp. Weigh accurately when cool.

Hang the smaller coil centrally in the larger and connect the voltameter in series with an ammeter and a bank of lamps to the 110 volt terminals, taking care that the larger coil is made anode. Note the duration of the electrolysis closely and read and record the ammeter every five minutes. If a current of two amperes be used, the electrolysis should be continued for half an hour; less current needs proportionately longer time.

At the close of the electrolysis note the current again, break the circuit and immediately remove the cathode. Dip in water, then in alcohol; dry, cool and weigh as before. The difference in weight gives the amount of copper deposited.

From the result calculate the weight of copper deposited by one ampere-hour and post the result opposite your name on the board. Compare the results obtained by the class with that calculated from Faraday's law; the differences may be due to errors in manipulation, or to *inaccuracies in the ammeters used*. Note that the coulometer is used to measure coulombs; the coulometer and the watch to measure currents, and thus to standardize ammeters; the legal definition of an ampere is "that current which will deposit 0.0011181 g. silver per second from a concentrated neutral silver nitrate solution".

EXERCISE 9

EFFECT OF CURRENT DENSITY. THE "LIMITING CURRENT"

In this exercise solutions of ferrous sulphate are electrolysed, measuring the current and the time, and the amounts of oxidation at the anode are determined.[1] So long as the current density at the anode is below a certain value called the "limiting anodic current density," which depends on the temperature, the rate of stirring, and the concentration and acidity of the electrolyte, every 96540 coulombs oxidize one equivalent of ferrous sulphate ($FeSO_4$; 151.96 grams). With higher current densities, however, oxygen is liberated at the anode (why?), and the amount of ferrous sulphate oxidized in a given time is practically independent of the current (why?).

The Apparatus

The anode, a lead cylinder covered with lead peroxide, is rotated (motor and belt) in a porous pot standing in a larger glass cylinder (battery jar); the cathode is a large sheet of lead surrounding the porous pot; the electrolyte in the porous pot is a solution of ferrous sulphate containing about 10% by volume of sulphuric acid; the electrolyte in the battery jar is 10% sulphuric acid. Before beginning the experiment, the height and diameter of the anode must be measured and its surface area calculated.

To "Form" the Anode.—Before carrying out the electrolyses the anode must be "formed," that is, covered with a matt brown surface of lead peroxide.[2] For this purpose fill the porous pot and battery jar with 10% sulphuric acid to the same level, completely covering the anode. Connect the cell, in series with ammeter lamp-rheostat and switch, to the 110 volt terminals and connect the motor direct to the same terminals. Start the motor, and send a current of about three amperes through the cell for about ten minutes.

(A) Electrolysis with Diaphragm; Rotating Electrode

Syphon out the contents of the porous pot and place in it a carefully measured volume (250 c.c. or 150 c.c. depending on the size of the pot) of the ferrous sulphate solution. Start the motor; adjust the lamp rheostat to give a current of

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[1] *Some members of the class will study the reduction of ferric sulphate at the cathode.*

[2] *Those working with ferric sulphate "form" the cathode similarly, covering it with a matt gray surface of metallic lead.*

[illegible]

[illegible]

[illegible]

[illegible]

[illegible]

[illegible]

[illegible]

[illegible]

[illegible]

[illegible]

about four amperes, and electrolyse for ten minutes, noting the current at the beginning and at 2½-minute intervals thereafter.

The Analysis.—(1) *During the electrolysis* fill one burette with decinormal solution of ferrous sulphate (do not use the electrolysis solution by mistake!) and the other with decinormal potassium permanganate. Determine the amount of ferrous sulphate in 10 c.c. of the stock solution used for electrolysis, following the directions given below. Check by duplicate titrations, and calculate the number of equivalents of ferrous sulphate in the measured volume of solution taken for electrolysis.

(2) *After the electrolysis is finished* titrate 10 c.c.[1] of the contents of the porous pot (in duplicate), and calculate the number of equivalents of ferrous sulphate oxidized during the electrolysis.

The Graph.—Taking "currents" as abscissae (x), and "equivalents oxidized in ten minutes" as ordinates (y), plot (*i*) the line $y=\frac{600}{96540}x$ and (*ii*) the point given by the experiment. It will be found that the point lies below the line—what conclusion can be drawn from this? Through the point draw a horizontal to cut the line; the abscissa corresponding to the point of intersection gives the "limiting current" (Why?). From the area of the anode calculate the "limiting anodic current density" for the conditions under which the electrolysis was performed.

Further Electrolyses of the Same Solution

Repeat the electrolysis with a fresh portion of the original solution, but using a different current. Enter the result on the graph. Four points at least should be determined; but results obtained from two different cells may be entered on the same graph if the rotating electrodes are driven at the same speed (from the same motor).

Electrolysis of a more Dilute Solution

Dilute the stock solution with 10% sulphuric acid to exactly double its volume, and electrolyse for ten minutes as before, each student with a different current. Plot.

Note the relation between concentration and limiting current.

Electrolysis with Bandaged Electrode

Slip the cylindrical bandage over the rotating electrode, and determine the limiting current.

How has the bandage affected the efficiency of the electrode as an oxidizing (or reducing) agent? How do you account for the effect of the bandage? Compare the effect of the adherent precipitate formed at the cathode in Exercise 3 when lime salts or chromates were added to the electrolyte.

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[1] *Those working at the reduction of ferric sulphate must take 25 c.c.*

(B) ELECTROLYSIS WITHOUT DIAPHRAGM; SHEET AND WIRE ELECTRODES

Cells are provided each consisting of a porcelain beaker lined with a sheet of lead which serves as one electrode, while a piece of lead wire suspended in the centre acts as the other. Connect two of these cells in series with a 16 c.p. carbon lamp, so that the sheet will be anode in one and cathode in the other.

Form the electrodes.

Measure into each cell 250 c.c. of the solution provided, which consists of water, sulphuric acid, ferrous sulphate, and ferric sulphate, the weights of iron in the two forms being about equal.

Electrolyse for about an hour with about 0.5 ampere, noting current and time.

By analysis of the original solution, and of the solution in the cell after electrolysis (take 25 c.c.), determine the amounts of iron oxidized or reduced.

Are the results such as might have been expected? The current used was greater than the limiting current for the large electrode; how might this have been ascertained?

NOTE.—THE VOLUMETRIC DETERMINATION OF FERROUS SALTS

A measured portion of the solution to be analyzed is put into a beaker, with approximately five or six times its volume of water; and a few drops of concentrated sulphuric acid are added. Decinormal potassium permanganate is then added from a burette until the liquid in the beaker acquires a permanent pink tinge. The decinormal ferrous sulphate in the other burette is used only for "titrating back." One litre of decinormal permanganate oxidizes one-tenth equivalent ferrous sulphate $= \frac{1}{10}Fe\ SO_4 = 15.196$ grams.

EXERCISE 10

ELECTROCHEMICAL PREPARATIONS

(A) PREPARATION OF CHROME YELLOW AND OF WHITE LEAD

When a solution of potassium chlorate containing potassium (or sodium) chromate is electrolysed between two lead plates, the anode dissolves forming lead chlorate solution, which then reacts with the chromate to form a precipitate of chrome yellow. If potassium (or sodium) carbonate be substituted for the chromate, the precipitate is white lead. The reactions may be represented thus:

$$Pb(ClO_3)_2 + K_2CrO_4 = 2KClO_3 + PbCrO_4 \text{ (chrome yellow)}$$

$$\begin{array}{l} Pb(ClO_3)_2 + 2KOH = 2KClO_3 + \\ Pb(ClO_3)_2 + K_2CO_3 = 2KClO_3 + \end{array} \left\{ \begin{array}{l} Pb(OH)_2 \\ PbCO_3 \end{array} \right\} \text{white lead}$$

If carbon dioxide gas is passed into the solution during electrolysis the percentage of lead carbonate ($PbCO_3$) in the white lead is increased. (Where does the "2KOH" come from?)

The apparatus.—The cell consists of two lead plates about $2\frac{1}{2}'' \times 3\frac{1}{2}''$ placed on opposite sides of a rectangular glass jar. It is to be connected in series with an ammeter, lamp-rheostat and switch, to the 110 volt terminals. The cell voltage is measured with a voltmeter and a small gas generator serves to supply the carbon dioxide for the white lead cell.

The electrolysis.—Connect up the circuit as indicated above, and fill the cell with the solution provided.[1] Allow a current of about half an ampere to flow, taking ammeter and voltmeter readings at five or ten minute intervals to get the average current and the potential difference. At the end of one hour stop the electrolysis, brush off as much as possible of the precipitate adhering to the anode, and collect with suction on a filter paper which has previously been well dried and weighed. Dry the filter paper containing the precipitate in the oven and weigh again.

Calculate the yield of chrome yellow or of white lead, as the case may be, per kilowatt-hour.

(B) PREPARATION OF AMMONIUM PERSULPHATE

When a saturated solution of ammonium sulphate $(NH_4)_2SO_4$ is electrolysed at low temperature and with a high anodic current density, the sulphate is oxidized to persulphate, $NH_4.SO_4$. Under certain conditions small amounts of hydrogen peroxide, H_2O_2, are also formed.

The apparatus.—The cell consists of a cylindrical glass or porcelain battery jar, containing a lead tube cathode coiled round a cylindrical porous pot. Within the pot is a sheet platinum anode of one square inch total area, and a coil of glass tubing. The glass and lead tubes are connected by a short piece of rubber tubing, and water from the tap is run through them to keep the electrolyte cool.

The electrolysis.—Fill the anode compartment with a measured volume of saturated ammonium sulphate solution, and the cathode compartment to about the same level with dilute sulphuric acid (1: 2 by vol.). Connect the electrodes in series with a lamp-rheostat ammeter and switch to the 110 volt terminals, and begin the circulation of cooling water. Allow a current of about 2 amperes to flow for 30 minutes, reading the ammeter at intervals of 3 min. to get the average current. During the electrolysis the flow of water should be so adjusted that the temperature of the electrolyte does not exceed 20° C.

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[1] *The electrolyte for chrome yellow contains 12g of potassium chlorate and 3g of potassium chromate per litre; that for white lead contains 12g of potassium chlorate and 3g of potassium carbonate per litre.*

10

The analysis.—During the electrolysis fill two burettes with decinormal ferrous sulphate and decinormal potassium permanganate respectively, and compare these solutions.

At the end of the electrolysis pipette 10 c.c. of the anolyte into a beaker containing 150 c.c. of dilute sulphuric acid (1: 9 by vol.), and add the permanganate until a permanent faint pink colour is produced. Then add a measured excess (about 50 c.c.) of the ferrous solution, allow to stand for about 5 minutes, determine the residual ferrous salt by titration with the permanganate, and subtract, to get the amount oxidized.

In the titration the amount of hydrogen peroxide formed is proportional to the amount of permanganate needed to produce the first permanent colour:

$$2KMnO_4+5H_2O_2+3H_2SO_4=K_4SO_4+2MnSO_4+8H_2O+5O_2$$

The amount of persulphate formed is proportional to the amount of ferrous sulphate oxidized:

$$2NH_4.SO_4+2FeSO_4=Fe_2(SO_4)_3+(NH_4)_2SO_4$$

Current efficiency.—From the current and time readings calculate the quantity of ammonium persulphate that would have been formed if every 96540 coulombs gave rise to one formula-weight $NH_4.SO_4$. Compare with the quantity actually formed, and calculate the current efficiency of the electrolysis regarded as a process for preparing ammonium persulphate. (These calculations are easily made if the quantities are expressed in *equivalents*. How many equivalents of ferrous salt, or of permanganate, are contained in one c.c. of the volumetric solutions employed?)

(C) OXIDATION OF CHROMIUM SULPHATE TO CHROMIC ACID

In this preparation a solution of potassium chromium sulphate containing sulphuric acid is electrolysed, the current and time are noted, and the amount of chromic acid formed is determined volumetrically.

The apparatus.—The anode, a lead cylinder covered with lead peroxide, rotates in a porous pot standing in a larger glass cylinder (battery jar). The cathode is a large sheet of lead surrounding the porous pot. The electrolyte in both the inner and outer compartments is a solution of chrome alum made by dissolving 200 g. of the crystals in hot water, adding 150 c.c. of concentrated sulphuric acid and making up the volume to one litre with water. The anode is "formed" as described in Ex. 9. (Chrome alum:—$K_2SO_4.Cr_2(SO_4)_3.24H_2O$).

The electrolysis.—Place 125 c.c. of electrolyte in the porous pot, and fill the outer cylinder to the same level with the same solution. Connect the cell in series with a lamp rheostat,

ammeter and switch to the 110 volt terminals. Start the stirring before closing the circuit through the cell. Pass a current of about one ampere for one hour and take ammeter readings at 5 minute intervals.

The analysis.—During the electrolysis, fill the burettes with decinormal potassium permanganate and decinormal ferrous sulphate solutions. At the end of the electrolysis add a measured excess of the ferrous sulphate solution to 10 c.c. of the anolyte in a beaker; dilute with water and determine the excess of ferrous sulphate by titration with the permanganate; subtract, to find the amount of ferrous salt oxidized by the chromic acid:

$$2\,CrO_3 + 6\,FeSO_4 + 6\,H_2SO_4 = Cr_2(SO_4)_3 + 3\,Fe_2(SO_4)_3 + 6\,H_2O$$

(What volume of the ferrous sulphate solution employed contains $6FeSO_4$?).

Current efficiency.—Calculate the current efficiency on the assumption that 96540 coulombs should yield one-third formula-weight of chromic oxide CrO_3. (How much ferrous sulphate would be oxidized by the same amount of electricity? How do these two quantities compare?)

(D) Reduction of Sodium Nitrate to Nitrite

Sodium nitrate ($NaNO_3$) is reduced at the cathode to sodium nitrite ($NaNO_2$) and this again to hyponitrite, hydroxylamine, and ammonia. Except with *copper* cathodes, the nitrite is more easily reduced than the nitrate itself, and only small amounts of the former remain in the electrolyte.

At the anode nitrites are easily oxidized, the solution becoming acid, and oxides of nitrogen being evolved; if the solution be kept alkaline, however, and an *iron* anode be used, very little oxidation takes place.

By taking advantage of the properties of these two metals, it is possible to obtain a good yield of nitrite without the use of a diaphragm. (What good would a diaphragm do?)

The apparatus.—The cell consists of a round porcelain or glass battery jar fitted with a copper gauze cathode and an iron wire spiral anode. (Why use wire?) An ammeter, a switch, and a lamp rheostat are also required.

The electrolyte.—20 g. sodium nitrate (much less than would be used in a technical preparation), 20 c.c. normal sodium hydrate solution, 20 c.c. half-normal copper nitrate solution, and enough ammonia to redissolve the precipitate first formed, are made up to one litre. The addition of copper to the electrolyte produces a spongy deposit of copper at the cathode which is particularly effective in reducing the nitrate, and thus sparing the nitrite.

The electrolysis.—Put a known volume (about 300 c.c.) of the electrolyte into the cell, and connect through ammeter and lamp rheostat to the 110 volt terminals. Allow a current of about one ampere to flow for one hour, taking readings of the ammeter every 5 minutes.

The analysis.—From a burette run a known quantity (about 10 to 15 c.c.) of tenth normal potassium permanganate solution into a beaker, dilute to about 200 c.c. with water, add about 2 or 3 c.c. of concentrated sulphuric acid, and warm to about 40° or 50° C. Then run in the cell solution from another burette until the colour is discharged. Towards the end of the titration the cell solution must be added slowly, as the discharge of the pink colour takes some time.

$$5NaNO_2 + 2KMnO_4 + 3H_2SO_4 = 5NaNO_3 + K_2SO_4 + 2MnSO_4 + 3H_2O$$

(How many grams of sodium nitrite are oxidized by one litre of decinormal permanganate?)

Current efficiency.—Assuming that 96540 coulombs yield one half formula weight of sodium nitrite, calculate the current efficiency of the electrolysis regarded as a method of preparation of sodium nitrite. (How much hydrogen gas would be required to prepare 0.5 $NaNO_2$ from sodium nitrate?)

TABLES OF ELECTROCHEMICAL DATA

I. Symbol, International Weight, Valency and Potential.

Aluminum	Al	27.11g.	$AlCl_3$	1.00 V.
Antimony	Sb	120.2	$SbCl_3$	< -0.743
Arsenic	As	75.0	$AsCl_3$	< -0.570
Barium	Ba	137.4	$BaCl_2$	2.54
Bismuth	Bi	208.5	$BiCl_3$	< -0.668
Bromine	Br	79.96	HBr	−1.270
Cadmium	Cd	112.4	$CdCl_2$	0.143
Calcium	Ca	40.04	$CaCl_2$	2.28
Carbon	C	12.00	H_2CO_3	
Chlorine	Cl	35.45	HCl	−1.694
Chromium	Cr	52.16	$CrCl_3$, H_2CrO_4*,	
Cobalt	Co	59.0	$CoCl_2$	−0.045
Copper	Cu	63.6	$CuCl$, $CuCl_2$	−0.606
Fluorine	F	19.0	HF	−2.24
Gold	Au	197.2	$AuCl$, $AuCl_3$	< -1.356
Hydrogen	H	1.008	HCl	−0.277
Iron	Fe	55.9	$FeCl_2$, $FeCl_3$	0.063
Iodine	I	126.86	HI	−0.797
Lead	Pb	206.9	$PbCl_2$, $PbCl_4$	−0.129
Lithium	Li	7.03	$LiCl$	
Magnesium . .	Mg	24.36	$MgCl_2$	2.26, 1.21
Manganese. . .	Mn	55.0	$MnCl_2$, $HMnO_4$	0.798
Mercury	Hg	200.0	$HgCl$, $HgCl_2$	−1.027
Nickel	Ni	58.7	$NiCl_2$	−0.049
Nitrogen.	N	14.04	NH_4Cl	
Oxygen	O	16.00	H_2O	−1.396
Phosphorus . .	P	31.02	H_3PO_3, H_3PO_4	
Platinum.	Pt	194.8	$PtCl_2$, $PtCl_4$	< -1.140
Potassium . . .	K	39.15	KCl	2.92
Silver	Ag	107.93	$AgCl$	−1.048
Sodium	Na	23.05	$NaCl$	2.54
Strontium	Sr	87.6	$SrCl_2$	2.49
Sulphur.	S	32.06	H_2S, H_2SO_4	
Thallium	Tl	204.1	$TlCl$	0.045
Tin	Sn	119.0	$SnCl_2$, $SnCl_4$	< -0.085
Zinc	Zn	65.4	$ZnCl_2$	0.493

*also $H_2Cr_2O_7$

II. Mobilities at 18° C.

$\phi =$	10^4	10^5	10^6	10^7	∞
K	55.8	61.3	63.7	64.7	65.3
Na	35.0	40.5	42.9	43.8	44.4
Li	26.1	31.6	34.0	34.9	35.5
NH_4	54.8	60.2	62.7	63.6	64.2
Ag	43.3	51.9	54.7	55.4	55.7
½ Ba	33.8	45.7	52.2	55.0	57.3
	....	....	47	53	57
½ Sr	30.5	42.4	48.9	51.7	54.0
	....	....	43	49	54
½ Ca	29.4	41.4	47.8	50.6	53.0
	....	31	44	49	53
½ Mg	25	37	43	47	49
	20	31	40	44	48
½ Zn	24.0	35.9	42.3	45.1	47.5
	17	27	38	43	47
½ Cu	....	....	....	....	....
	15	27	41	47	49
½ Cd	....	....	....	....	....
	13	26	37	....	....
H	296	310	314	316	318
Cl	56.5	62.0	64.4	65.3	65.9
I	57.3	62.7	65.1	66.1	66.7
NO_3	51.4	56.8	59.3	60.2	60.8
ClO_3	43.2	51.3	54.1	55.5	56.2
$C_2H_3O_2$	26.4	30.8	32.6	33.1	33.7
½ SO_4	41.9	56.1	64.0	67.2	69.7
	30	46	60	66	70
½ C_2O_4	39	51	58	61	63
	....	....	56	61	63
½ CO_3	38	55	69	....	....
OH	157	167	171	172	174

NOTE.—Where two series of values are given, the lower line is to be used in calculating Λ for solutions containing bivalent ions only, *e.g.* $CuSO_4$, $ZnSO_4$; the upper line in all other cases.

TABLES OF ELECTROCHEMICAL DATA

III. Conductivity, Transport and Mobility of the Anion, at 18° C.

		Λ	Λ	Λ	Λ	H	u
	ϕ =	10^4	10^5	10^6	10^7	10^4	10^4
KCl	obs.	112	123	128	130	.51	57
	calc.	112	123	128	130	.51	57
KI	obs.	114	124	129	130	.51	58
	calc.	113	124	129	135	.51	57
KNO_3	obs.	104	118	123	125	.50	52
	calc.	107	118	123	125	.48	51
NH_4Cl	obs.	111	122	127	129	.51	57
	calc.	111	122	127	129	.51	57
NaCl	obs.	93	103	108	110	.62	57
	calc.	92	102	107	109	.62	59
$NaC_2H_3O_2$	obs.	61	70	75	77	.44	27
	calc.	61	71	75	77	.42	26
$AgNO_3$	obs.	95	109	114	116	.53	50
	calc.	95	109	114	116	.54	57
$\frac{1}{2}$ $ZnCl_2$	obs.	82	98	107	110	.56	46
	calc.	81	98	107	110	.63	51
$\frac{1}{2}$ $ZnSO_4$	obs.	46	73	98	109	.59	27
	calc.	47	73	98	109	.63	30
$\frac{1}{2}$ $CuSO_4$	obs.	45	72	102	113	.63	28
	calc.	45	73	101	113	.67	30
HCl	obs.	351	370	377	...	.17	60
	calc.	352	372	378	381	.10	57
$\frac{1}{2}$ H_2SO_4	obs.	225	308	361	...	.19	43
	calc.	338	366	378	383	.12	42
$C_2H_4O_2$	obs.	4.6	14.3	41	107	.33	1.5
	calc.	322	341	347	349	.08	26
KOH	obs.	213	228	234	...	.74	158
	calc.	213	228	235	238	.74	158
NaOH	obs.	183	200	208	...	.82	150
	calc.	192	207	214	216	.82	157
NH_4OH	obs.	3.3	9.6	28	66	.56	1.8
	calc.	212	227	234	236	.84	157

Note.—The numbers after 'obs' give the results of experiment; those after 'calc' are calculated from the data of table II.

Table IV.—Specific Conductivities of Potassium Chloride Solutions

t	KCl normal		KCl $\frac{1}{10}$N		KCl $\frac{1}{50}$N		KCl $\frac{1}{100}$N	
	κ		κ		κ		κ	
0°	0,06541	172	0,00715	21	0,001521	45	0,000776	24
1	06713	173	0736	21	1566	46	0800	24
2	06886	175	0757	22	1612	47	0824	24
3	07061	176	0779	21	1659	46	0848	24
4	07237	177	0800	22	1705	47	0872	24
5	07414	179	0822	22	1752	48	0896	25
6	07593	180	0844	22	1800	48	0921	24
7	07773	181	0866	22	1848	48	0945	25
8	07954	182	0888	23	1896	49	0970	25
9	08136	183	0911	22	1945	49	0995	25
10	08319	185	0933	23	1994	49	1020	25
11	08504	185	0956	23	2043	50	1045	25
12	08689	187	0979	23	2093	49	1070	25
13	08876	187	1002	23	2142	51	1095	26
14	09063	189	1025	23	2193	50	1121	26
15	09252	189	1048	22	2243	51	1147	26
16	09441	190	1072	23	2294	51	1173	26
17	09631	191	1095	24	2345	52	1199	26
18	09822	192	1119	24	2397	52	1225	26
19	10014	193	1143	24	2449	52	1251	27
20	10207	193	1167	24	2501	52	1278	27
21	10300	194	1191	24	2553	53	1305	27
22	10594	195	1215	24	2606	53	1332	27
23	10789	195	1239	25	2659	53	1359	27
24	10984	196	1264	24	2712	53	1386	27
25	11180	197	1288	25	2765	54	1413	28
26	11377	197	1313	24	2819	54	1441	27
27	0,11574		1337	25	2873	54	1468	28
28			1362	25	2927	54	1496	28
29			1387	25	2981	55	1524	28
30			0,01412		0,003036		0,001552	

Normal Potassium Chloride Solution contains 74.59 g. of Potassium Chloride in one litre of solution at 18° C.

Table V.—Specific Conductivities of other Standard Solutions for Determining the Resistance-Capacity of Conductivity Vessels.

t	H_2SO_4 (max.)		$MgSO_4$ (max.)		NaCl (saturated)	
	κ		κ		κ	
0°	0,5184	120	0,02877	102	0,1345	41
1	5304	121	2979	104	1386	41
2	5425	122	3083	105	1427	42
3	5547	122	3188	106	1469	43
4	5669	123	3294	108	1512	43
5	5792	123	3402	110	1555	44
6	5915	123	3512	111	1599	44
7	6038	123	3623	112	1643	45
8	6161	124	3735	114	1688	46
9	6285	123	3849	114	1734	45
10	6408	124	3963	116	1779	47
11	6532	124	4079	118	1826	46
12	6656	124	4197	118	1482	47
13	6780	124	4315	119	1919	47_7
14	6904	124	4434	121	1966_7	47_9
15	7028	123	4555	121	2014_6	48_3
16	7151	124	4676	123	2062_9	48_6
17	7275	123	4799	123	2111_5	49_0
18	7398	124	4922	124	2160_5	49_4
19	7522	123	5046	125	2209_9	49_7
20	7645	123	5171	126	2259_6	50_0
21	7768	122	5297	127	2309_6	50_4
22	7890	123	5424	127	2360_0	51
23	8013	122	5551	128	2411	51
24	8135	122	5679	129	2462	51
25	8257	121	5808	129	2513	52
26	8378	121	5937	130	2565	51
27	8499	121	6067	130	2616	53
28	8620	120	6197	131	2669	52
29	8740	120	6328	131	2721	53
30	0,8860		0,06459		0,2774	

t	κ
KCl 21%	
$s_{18/4}$	=1,14081
17°	0,2771
18	2817
19°	2864
KNO_3 10%	
$s_{15/4}$	=1,06418
16°	0,08048
17	8217
18°	8386
K_2SO_4 10%	
$s_{20/4}$	=1,08150
17°	0,08428
18	8602
19°	8776
Gypsum (saturated)	
15°	0,001742
16	1791
17	1841
18	1891
19	1940
20	1990
21°	2039

CONVERSION TABLES.

[The numbers in square brackets are logarithms.]

Mathematical Constants.

$\pi = 3.1416$ [0.4971].
$e = 2.7183$ [0.4343].
log. nat. $x = 2.3026 \log_{10}x$ [0.3621].
$\log_{10}x = 0.4343$ log. nat. x [$\bar{1}.6378$].

Units of Energy.

one **erg** (c.g.s. unit) = 10^{-7} joules [$\bar{7}.0000$].
one **joule** (Electrical unit) = 10^7 ergs [7.0000] = 10198 g-cm. [4.0085 = 0.2382 cal. [$\bar{1}.3769$].
one **gram-centimeter** (Gravity unit) = 980.6 ergs [2.9915] = 980.6×10^{-7} joules [$\bar{5}.9915$] = 2.3409×10^{-5} cal. [$\bar{5}.3693$].
one **foot-pound** = 13825.5 g-cm. [4.1406].
one **cal.** = 18° C. gram calorie (Thermal unit) = 41890000 ergs [7.6221] = 4.189 joules [0.6221] = 42720 g-cm. [4.6306].
one Cal. = 10K = 1000 cal.
one **B.T.U.** (British thermal unit) = 252 cal. [2.4014].

Units of Force (energy per unit length).

one **dyne** (c.g.s. unit) = one erg per centimeter.
one **gram weight** = 980.6 dynes [2.9915].

Units of Power (energy per unit time).

one **watt** (Electrical unit) = 1 joule per second = 10^7 ergs per second = 0.2382 cal. per second [$\bar{1}.3769$].
one **horsepower** = 745.7 watts [2.8725] = 33000 foot-pounds per minute [4.5185].

Electrical Units.

volts × amperes × seconds = **joules.**
volts × amperes = **watts.**
amperes × seconds = **coulombs.**
Faraday's constant = 96540 [4.9847].

Weights and Measures.

one **pound** avoirdupois = 453.6 grams [2.6566].
one **ounce** avoirdupois = 28.35 grams [1.4525].
one **foot** = 30.48 cm. [1.4840].
one **cubic foot** = 28.317 litres [1.4520] = 6.229 imp. gal. [0.7944].
one imperial **gallon** = 4.546 litres [0.6576] = 1.201 U.S. gal. [0.0795] = 10 lbs. water at 16°.7 C.
one **U.S. gallon** = 3.7854 litres [0.5781] = 0.8327 imp. gal. [$\bar{1}.9205$].

Gas Laws.

The relation between P = pressure in mm. mercury, V = vol. in c.c., and t = temp. in degrees Centigrade, is given by

$$PV = 62370N(t+273) \quad [4.7949].$$

Where N = (weight of gas in grams) divided by (formula weight of gas).

If the pressure be expressed in grams per cm^2 instead of in mm., the factor 84760 [4.9282] must be used instead of 62370: and if the pressure be expressed in units of 42720 gms. per cm^2, the factor 1.985 [0.2977] must be used.

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